Reviewer	Manying Xue, Chemist RAB3/HED (7509C)	Date: 07/22/04
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This DER was originally prepared under contract by Dynamac Corporation (20440 Century Boulevard, Suite 100; Germantown, MD 20874; submitted 02/26/2004). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

45645804 Schulz, H. (2002) Determination of the Residues of BAS 500 F and BAS 510 F in Apples and Processed Products Following Treatment with BAS 516 01 F Under Field Conditions in Germany 2001: Final Report: Study Code: IF-101/14264-00: BASF Registration Document Number 2001/1015047. Unpublished study prepared by BASF Agro Research. 107 p.

EXECUTIVE SUMMARY:

BASF Corporation has submitted an apple processing study. Four field trials were conducted in Germany. Apple samples were harvested 0 and/or 13-15 days following the last of four foliar spray applications of BAS 500 02 F (a "suspo-emulsion" (SE) formulation containing 100 g pyraclostrobin/L) at ~0.3 lb ai/A/application, with a 7- to 10-day retreatment interval, for a total rate of ~1.2 lb ai/A. Applications were made in ~103-110 gal/A of water. The SE formulation used on the apple processing study also contained another experimental active ingredient (BAS 510 F) as part of the tank-mix; data for the BAS 510 F active ingredient are not reviewed herein. Apple samples were processed into fresh pomace and juice (Processing I) or fresh and dried pomace, thick juice, juice, and apple sauce (Processing II) using simulated commercial processing procedures. According to OPPTS 860.1000, Table 1, the significant processed commodities of apple are wet pomace and juice; therefore, data for the additional processed commodities are presented for informational purposes, but are not discussed further.

Samples of apples and apple processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using LC/MS/MS, BASF Method Number 445/0. The method limit of quantitation (LOQ) was 0.02 ppm for each analyte (pyraclostrobin and BF 500-3) in/on all apple matrices. This method is adequate for data collection based on acceptable concurrent method recovery data.

The maximum storage intervals of processing study samples from collection to analysis were 3.7 months for apple and 4.0 months for apple processed commodities. No storage stability data have been submitted with this petition. Available storage stability data indicated that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for apple and apple processed samples for this study (D269668, etc., L. Cheng, 11/28/2001).

The combined residues were <0.153-0.699 ppm in the RAC. The processing data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 did not concentrate in apple (fresh) juice; and concentrated in apple pomace at 9.6x (average of six samples: 7.3x, 14.4x, 6.5x,4.1x, 15.7x, and 9.7x).

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the apple processing study residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D290342.

COMPLIANCE:

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported.

A. BACKGROUND INFORMATION

Pyraclostrobin is a fungicide that is structurally related to the naturally occurring strobilurins, compounds derived from some fungal species. Pyraclostrobin is also in the same chemical class as azoxystrobin (PC 128810), registered for many crops and turf/lawn, and trifloxystrobin (PC 129112) which recently was granted a “reduced risk” status as a fungicide on many crops. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi.

TABLE A.1. Test Compound Nomenclature	
Compound	Chemical Structure
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use product/EPs	20% water dispersible granular formulation (WG; product name: Cabrio™ EG Fungicide; EPA Reg. No. 7969-187/EPA File Symbol 7969-RIT).

Pyraclostrobin technical is a white to light beige solid.

TABLE A.2. Physicochemical Properties		
Parameter	Value	Reference[1]
Melting point	63.7-65.2 °C	D269848 & D274191
Density	1.285g/cm^3 at 20°C	D269848 & D274191
Water solubility (20°C)	2.41 mg/L in deionized water at 20°C 1.9 mg/L in buffer system pH 7 at 20°C 2.3 mg/L in buffer system pH 4 at 20°C 1.9 mg/L in buffer system pH 9 at 20°C	D269848 & D274191
Solvent solubility (mg/L at 20°C)	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (≥110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L);	D269848 & D274191

TABLE A.2. Physicochemical Properties		
Parameter	Value	Reference[1]
	DMF (≥62 mg/L).	
Vapour pressure at 25°C	2.6 x 10^{-10} hPa (at 20°C); 6.4 x 10^{-10} hPa	D269848 & D274191
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D269848 & D274191
Octanol/water partition coefficient Log(K_{OW})	n-Octanol/water partition coefficient (K_{ow}) at room temperature (=K_{ow} of 3.80, pH 6.2; =log K_{ow} 4.18, pH 6.5).	D269848 & D274191

[1] Product Chemistry data were reviewed by the Registration Division (D269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak)

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

TABLE B.1.2. Study Use Pattern.

Location (City, Country; Year)	EP[1]	Application					Tank Mix Adjuvants
		Method; Timing	Vol (GPA[2])	Rate (lb ai/A)	RTI[3] (days)	Total Rate (lb ai/A)	
Lower Saxony, Germany; 2001 AT-01/020-1	SE	1: Broadcast foliar; 78 BBCH	106	0.268	--	1.076	None
		2: Broadcast foliar; 79 BBCH	107	0.271	8		
		3: Broadcast foliar; 81 BBCH	107	0.269	10		
		4: Broadcast foliar; 87 BBCH	106	0.268	9		
Thuringia, Germany; 2001 AT-01/020-2	SE	1: Broadcast foliar; 79 BBCH	106	0.268	--	1.093	None
		2: Broadcast foliar; 81 BBCH	109	0.275	8		
		3: Broadcast foliar; 83 BBCH	110	0.279	8		
		4: Broadcast foliar; 85 BBCH	107	0.271	7		
Schleswig-Holstein, Germany; 2001 AT-01/020-3	SE	1: Broadcast foliar; 78 BBCH	106	0.267	--	1.067	None
		2: Broadcast foliar; 78 BBCH	106	0.267	8		
		3: Broadcast foliar; 81 BBCH	106	0.267	10		
		4: Broadcast foliar; 87 BBCH	105	0.266	9		
Hesse, Germany; 2001 AT-01/020-4	SE	1: Broadcast foliar; 78-79 BBCH	107	0.269	--	1.062	None
		2: Broadcast foliar; 79 BBCH	104	0.264	8		
		3: Broadcast foliar; 81 BBCH	106	0.268	8		
		4: Broadcast foliar; 81-85 BBCH	103	0.261	8		

[1] EP = End-use Product; a “suspo-emulsion” (SE) formulation containing 100 g pyraclostrobin/L was used.
[2] GPA = Gallons per acre
[3] RTI = Retreatment Interval

B.2. Sample Handling and Processing Procedures

Two trials included an untreated plot for controls from each control plots a single untreated apple sample was collected at 0 and 14 days following the time of the last application. Single or duplicate treated samples of apple were collected from all trials 0 and 13-15 days after the last application. Samples collected for direct residue analysis of the RAC and for processing by Processing I weighed ≤7 kg, while bulk samples for Processing II weighed 70-91.2 kg. Samples for direct residue analysis were frozen on the day of harvest and transported to Institute Fresenius (Taunusstein, Germany), where they were homogenized and frozen until shipment to BASF AG (Limburgerhof, Germany) for residue analysis. Samples for processing were transported, on the day of collection, to Forschungsanstalt Geisenheim (Geisenheim, Germany) for processing, where they were stored at ambient conditions until processing.

Two processing procedures, simulating industrial procedures, were followed. Apples collected at the 0-day PHI from two trials were processed into fresh pomace and juice using Processing I. Apples collected at the 13/15-day PHI were processed into fresh and dried pomace, juice, apple sauce, and by-products using Processing II. Processing was completed within 5 days of harvest.

Briefly, using Processing I, apples were washed with water, transferred to a grater, and cut in small strips. Pulp was collected from under the grater, combined with any pulp remaining in the grater, and transferred to a hydraulic press. The pulp was pressed against the filter cloth forcing the juice through the cloth. The resulting pomace was collected, and the juice was pasteurized at 90 °C for 30 minutes prior to collection.

Using Processing II, apples were washed and the pulp was collected as described above. A subsample of pulp was used for processing to apple sauce and the remaining pulp was used for processing apple juice and pomace through a rack and cloth press. The pressed juice was passed through a sieve and the coarse particles combined with the fresh pomace. A subsample of fresh pomace was dried to a weight of at least 85% and dried pomace was collected. The sieved juice was clarified with pectinase, gelatin and Kieselsol were added, and the solution cross-flow filtered. Thick juice was collected and the clear juice was pasteurized as described above. The pulp for apple sauce was heated to 85 °C, the resulting mash was strained through a puree apparatus, and apple sauce was collected. The mash remaining in the puree apparatus was collected as “the remainder of the straining process”.

Adequate descriptions and material balance information were submitted for the processing procedures. The RAC and processed samples were frozen (≤-18 °C) and shipped to Institute Fresenius (Taunusstein, Germany) and later to BASF AG (Limburgerhof, Germany) for residue analysis.

B.3. Analytical Methodology

Samples of apple and its processed fractions were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using LC/MS/MS, BASF Method Number 445/0. A brief description of the method was included in the submission. BASF Method Number 445/0 is similar to the proposed enforcement method (LC/MS/MS BASF Method Number D9808) submitted in conjunction with a previous pyraclostrobin petition (PP#0F06139; DP Barcodes D269668, etc., L. Cheng, 11/28/01). Using Method 445/0 apple commodities were extracted with a mixture of methanol, water, and hydrochloric acid and partitioned with cyclohexane; dried pomace was extracted with methanol. Residues of pyraclostrobin and its metabolite BF 500-3 are analyzed by LC/MS/MS. For quantitation, the product/daughter ion for the transition m/z 388 → 194 for pyraclostrobin (BAS 500 F) and m/z 358 → 164 for BAS 500-3 are measured. The method limit of quantitation (LOQ) was 0.02 ppm for each analyte (pyraclostrobin and BF 500-3) in/on all apple matrices.

C. RESULTS AND DISCUSSION

Sample storage intervals and conditions are summarized in Table C.2. Apples and the processed apple commodities were frozen following processing until analysis. The maximum storage intervals of processing study samples from collection to analysis were 3.7 months for apple and 4.0 months for apple processed commodities. No storage stability data have been submitted with this petition. Available storage stability data indicated that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for apple and apple processed samples for this study (D269668, etc., L. Cheng, 11/28/2001).

Concurrent recovery data from the apple processing study are presented in Table C.1. Residues of pyraclostrobin and its metabolite BF 500-3 in/on apple and its processed commodities including wet pomace and juice were quantitated using LC/MS/MS, BASF Method 445/0. The method LOQ was 0.02 ppm for each analyte. This method is adequate for data collection based on acceptable concurrent method recovery data. Apparent residues of pyraclostrobin and its metabolite BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on two samples of untreated apple fruit (RAC) and one sample each of wash water, washed fruit, fresh and dried pomace, thick and fresh juice, apple sauce, and the straining remainder processed from untreated apples.

Residue data from the apple processing study are reported in Table C.3. According to OPPTS 860.1000, Table 1, the significant processed commodities of apple are wet pomace and juice; therefore, data for the additional processed commodities are presented for informational purposes in Table C.3., but are not discussed further. The processing data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 did not concentrate in all apple (fresh) juice; and concentrated in apple pomace at 9.6x (average of six samples: 7.3x, 14.4x, 6.5x, 4.1x, 15.7x, and 9.7x).

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin and its Metabolite BF 500-3 from Apple and Processed Apple Commodities.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean Recovery ± sd (%)
Pyraclostrobin				
Apple, whole fruit	0.02	2	90.94, 95.01	93.89 ± 7.25
	2.0	2	86.25, 103.34	
Washed apple	0.02	1	94.36	88.43
	2.0	1	82.50	
Wash water	0.02	1	99.80	100.23
	2.0	1	100.65	
Fresh pomace	0.02	1	95.84	88.58

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin and its Metabolite BF 500-3 from Apple and Processed Apple Commodities.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean Recovery ± sd (%)
	2.0	1	81.31	
Dried pomace	0.02	1	93.14	97.35
	2.0	1	101.56	
Fresh juice	0.02	1	72.93	64.49
	2.0	1	56.04	
Thick juice	0.02	1	92.15	86.43
	2.0	1	80.71	
Apple sauce	0.02	1	68.81	76.84
	2.0	1	84.87	
Remainder of straining process	0.02	1	99.34	88.01
	2.0	1	76.68	
BF 500-3				
Apple, whole fruit	0.02	2	83.91, 89.26	86.05 ± 3.23
	2.0	2	82.71, 88.33	
Washed apple	0.02	1	89.13	88.06
	2.0	1	86.98	
Wash water	0.02	1	117.31	110.66
	2.0	1	104.00	
Fresh pomace	0.02	1	96.49	96.20
	2.0	1	95.91	
Dried pomace	0.02	1	91.32	100.06
	2.0	1	108.80	
Fresh juice	0.02	1	84.07	77.61
	2.0	1	71.14	
Thick juice	0.02	1	97.73	93.86
	2.0	1	89.98	
Apple sauce	0.02	1	72.30	72.50
	2.0	1	72.70	
Remainder of straining process	0.02	1	68.72	74.59
	2.0	1	80.46	

TABLE C.2. Summary of Storage Conditions

Matrix	Storage Temp. (°C)	Actual Storage Duration (days) [1]	Interval of Demonstrated Storage Stability [2]
Apple	≤-18	89-111 days (2.9-3.7 months)	The available storage stability data indicate that residues of pyraclostrobin and its
Washed fruit		88-101 days (2.9-3.3 months)	

TABLE C.2. Summary of Storage Conditions

Matrix	Storage Temp. (°C)	Actual Storage Duration (days) [1]	Interval of Demonstrated Storage Stability [2]
Pomace, wet and dried		96-123 days (3.2-4.0 months)	metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months.
Juice, fresh and thick		89-112 days (2.9-3.7 months)	
Apple sauce		91-104 days (3.0-3.4 months)	

[1] Apples were processed within 1-5 days of harvest; all samples were analyzed within 0-4 days of extraction.
[2] Refer to storage stability data reviewed in conjunction with a previous pyraclostrobin petition (PP#0F06139; DP Barcode D269668, etc., L. Cheng, 11/28/01).

TABLE C.3. Residue Data from Apple Processing Study with Pyraclostrobin.

RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)			Processing Factor		
				Pyraclostrobin	BF 500-3	Total	Pyraclostrobin	BF 500-3	Total
Apple 01/020-1	RAC	1.076	0	0.267	0.028	0.295	--	--	--
	wash water			0.082	<0.02	<0.102	0.3x	0.7x	0.3x
	fresh pomace			1.896	0.268	2.163	7.1x	9.6x	7.3x
	juice			<0.02	<0.02	<0.04	0.1x	0.7x	0.1x
	RAC	1.076	14	0.165	0.039	0.204	--	--	--
	wash water			<0.02	<0.02	<0.04	0.1x	0.5x	0.2x
	washed fruit			0.139	<0.02	<0.159	0.8x	0.5x	0.8x
	fresh pomace			2.445	0.484	2.928	14.8x	12.4x	14.4x
	dried pomace			8.407	1.805	10.212	51.0x	46.3x	50.1x
	thick juice			0.020	<0.02	<0.040	0.1x	0.5x	0.2x
	fresh juice			<0.02	<0.02	<0.04	0.1x	0.5x	0.2x
	apple sauce			0.062	<0.02	<0.082	0.4x	0.5x	0.4x
	straining remainder			0.534	0.135	0.669	3.2x	3.5x	3.3x
Apple 01/020-2	RAC	1.093	0	0.835	0.097	0.933	--	--	--
	RAC	1.093	14	0.555	0.144	0.699	--	--	--
	wash water			0.072	<0.02	<0.092	0.1x	0.1x	0.1x
	washed fruit			0.233	0.074	0.308	0.4x	0.5x	0.4x
	fresh pomace			3.545	1.005	4.550	6.4x	0.7x	6.5x
	dried			7.774	2.475	10.248	14.0x	17.2x	14.7x

TABLE C.3. Residue Data from Apple Processing Study with Pyraclostrobin.

RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)			Processing Factor		
				Pyraclostrobin	BF 500-3	Total	Pyraclostrobin	BF 500-3	Total
	pomace								
	thick juice			0.020	<0.02	<0.040	<0.1x	0.1x	0.1x
	fresh juice			<0.02	<0.02	<0.04	<0.1x	0.1x	0.1x
	apple sauce			0.228	0.046	0.274	0.4x	0.3x	0.4x
	straining remainder			1.083	0.221	1.304	2.0x	1.5x	1.9x
Apple 01/020-3	RAC	1.067	0	0.518	0.048	0.565	--	--	--
	wash water			0.026	<0.02	<0.046	0.1x	0.4x	0.1x
	fresh pomace			2.100	0.233	2.333	4.1x	4.9x	4.1x
	juice			<0.02	<0.02	<0.04	<0.1x	0.4x	0.1x
	RAC	1.067	13	0.266	0.034	0.300	--	--	--
	wash water			<0.02	<0.02	<0.04	0.1x	0.6x	0.1x
	washed fruit			0.301	0.044	0.345	1.1x	1.3x	1.2x
	fresh pomace			4.258	0.448	4.706	16.0x	13.2x	15.7x
	dried pomace			11.356	1.351	12.707	42.7x	39.7x	42.4x
	thick juice			<0.02	<0.02	<0.04	0.1x	0.6x	0.1x
	fresh juice			<0.02	<0.02	<0.04	0.1x	0.6x	0.1x
	apple sauce			0.178	<0.02	<0.198	0.7x	0.6x	0.7x
	straining remainder			0.882	0.060	0.942	3.3x	1.8x	3.1x
Apple 01/020-4	RAC	1.062	0	0.179	<0.02	<0.199	--	--	--
	RAC	1.062	15	0.133	<0.02	<0.153	--	--	--
	wash water			<0.02	<0.02	<0.04	0.2x	1x	0.3x
	washed fruit			0.110	<0.02	<0.130	0.8x	1x	0.8x
	fresh pomace			1.314	0.168	1.482	9.9x	8.4x	9.7x
	dried pomace			4.165	0.592	4.757	31.3x	29.6x	31.1x
	thick juice			<0.02	<0.02	<0.04	0.2x	1x	0.3x
	fresh juice			<0.02	<0.02	<0.04	0.2x	1x	0.3x
	apple sauce			0.087	<0.02	0.107	0.7x	1x	0.7x
	straining			0.144	<0.02	0.164	1.1x	1x	1.1x

TABLE C.3. Residue Data from Apple Processing Study with Pyraclostrobin.									
RAC	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)			Processing Factor		
				Pyraclostrobin	BF 500-3	Total	Pyraclostrobin	BF 500-3	Total
	remainder								

D. CONCLUSION

The processing data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 did not concentrate in all apple (fresh) juice; and concentrated in apple pomace at 9.6x (average of six samples: 7.3x, 14.4x, 6.5x, 4.1x, 15.7x, and 9.7x).

The average processing factor of 9.6x for apple wet pomace is less than the maximum theoretical concentration factor of >14x for apples and maximum observed (experimental) concentration factor of 14x for apple pomace (OPPTS 860.1520, Tables 1 and 4). However, the maximum observed processing factor of 15.7x for wet pomace exceeds the maximum observed (experimental) concentration factor of 14x for apple pomace (OPPTS 860.1520, Table 4).

E. REFERENCES

DP Barcodes:	D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, and D278429
Subject:	PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS #175013-18-0.
From:	L. Cheng
To:	C. Giles-Parker/J. Bazuin
Dated:	11/28/01
MRIDs:	45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI:ChemTeam:06/29/04:L.Cheng: 07/22/04
Petition Number(s): PP#2F06431
DP Barcode(s): D290342, D290343, and D290369
PC Code: 099100

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